

On optimal values of α for the analytic Hartree-Fock-Slater method

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(Dated: February 2, 2008)

We have examined the performance of the analytic Hartree-Fock-Slater (HFS) method for various α values and empirically determined the optimal α value by minimizing the mean absolute error (MAE) in atomization energies of the G2 set of molecules. At the optimal α the HFS method's performance is far superior with the MAE of 14 kcal/mol than that of the local density approximation (MAE \sim 36 kcal/mol) or the Hartree-Fock theory (MAE \sim 78 kcal/mol). The HFS exchange functional with $\alpha = 0.7091$ performs significantly better than the Kohn-Sham exchange functional for equally weighted atoms H-Kr. We speculate that use of this single α value may be useful in parametrization of empirical exchange-correlation functionals.

PACS numbers:

Keywords: analytic density functional theory, exchange potential, Slater's $X\alpha$, Hartree-Fock-Slater

The problems with numerical integration in quantum mechanical calculations are well known.^{1,2} Thus, all *ab initio* electronic structure calculations can be divided into two classes. In the first class, historically called *ab initio*, all quantum mechanical matrix elements are computed to machine precision.³ The second class of electronic structure calculations require numerical integration and machine-precision matrix elements are totally impractical, and thus, except for atoms, machine-precision energies are out of the question. Until very recently this second class included almost all density-functional calculations.⁴ Recently, fully analytic Hartree-Fock-Slater⁵ (HFS) variant of the density functional theory (DFT) was implemented using Gaussian basis sets.¹ This approach employs fitting of the potential to integrable functional form, rather than by fitting or integration on numerical grid. The technique is computationally very efficient in comparison with the grid-based implementation and provides smooth potential energy surfaces and exact energy gradients.¹ We have recently extended this scheme to allow for the atom-dependent exchange parameters α that scale the exchange potential by means of a muffin-tin (MT)-like approach.⁶ In our method matrix elements are computed to machine accuracy. Further, in contrast to earlier MT implementation, here the energy is both meaningful and stationary. One can require that atoms dissociate into their exact experimental rather than approximate Hartree-Fock (HF) electronic energies. This approach⁷ when applied to a standard set of molecules that are used in performance tests of DFT models yields results that are intermediate between either the local density approximation (LDA) or the HF approximation and more sophisticated hybrid or generalized gradient approximations (GGA).⁸

In the HFS⁵ model, the *nonlocal* exchange potential in the Hartree-Fock method is replaced by a *local* exchange

potential that is given by

$$v_x(\vec{r}) = -\frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} \alpha \rho^{1/3}. \quad (1)$$

Here, the parameter α , called Slater's statistical exchange parameter, is unity. Similar expression for the exchange energy of the homogeneous electron gas was obtained earlier by Dirac.⁹ Later, Gáspár¹⁰ and Kohn-Sham¹¹ (GKS) obtained the value of 2/3 for α by variationally minimizing the total energy functional. In the following years, α was taken purely as an adjustable parameter to obtain desired atomic properties.^{12,13,14,15} The first¹⁶ HFS calculations with meaningful numerically integrated total energies used a uniform α value of 0.7. Since then the HFS method has come to mean this α value. Later, the electronic structure calculations using the LDA by showed that the LDA give similar¹⁷ but not superior¹⁸ binding energies to the HFS method. Several studies since then have shown that the LDA has a general tendency to overbind.¹⁹

HF theory being analytic allows cheap geometry optimization despite its N^4 cost. In an analytic method one optimizes tens of linear-combination-of-atomic-orbital parameters per atom, rather than hundreds of plane-waves per pseudoatom, or thousands of numerical integration points per all-electron atom. With or without the MT-like advance, an N^3 analytic method might prove to be a practical geometry-optimization tool if appropriate choice(s) of the exchange parameter(s) is(are) made. In this article we asses the performance of analytic HF model for the GKS and the Slater values of α by computing the mean absolute error (MAE) in atomization energies of a set of 56 molecules (G2 set). We then determine the optimal value of α by minimizing the MAE for the G2 set of molecules. The calculations are performed for various basis sets in order to study the basis set dependence of the optimal α value. Our calculations show that the analytic HFS model with the optimal α

value performs better than the HF theory or the LDA and hence provides a computationally efficient scheme to study large systems at modest accuracy. Furthermore, by minimizing the MAE between the HF and the HFS total energies for atoms H through Kr, we find that best performance of the exchange functional in Eq.(1) is obtained for $\alpha = 0.7091$.

Our calculations in the Slater-Roothaan (SR) method require using the Gaussian basis sets to fit the orbitals and the Kohn-Sham potential. We have used the valence triple- ζ (TZ) 6-311G**^{20,21} and the DGauss²² valence double- ζ ²³ basis set (DZVP) for the orbitals. The *s*-type fitting bases are obtained by scaling the *s*-part of the orbital basis.²⁴ For the non-zero angular momentum components the resolution-of-the-identity-J (RI-J)²⁵ and A2²² basis sets are used for the Kohn-Sham potential fitting. Thus, four sets 6311G**/RI-J, 6311G**/A2, DZVP/RI-J, and DZVP/A2 of bases were used for optimizing the α value. The molecules were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm.²⁶ The α minimization was performed using powerful Perl scripts that drive the analytic DFT code.

Our first attempt to determine the optimal α is based on the atomic calculation. These calculations are numerical and therefore are free from the basis sets effects. Here we minimize the MAE in the HF and the HFS total energies for atoms H through Ar. The minimum occurs for $\alpha = 0.7267$ with the MAE of 0.101 a.u. The optimal α value decreases slightly to 0.7091 when the target set is extended to include the atoms up to krypton. At this value the MAE is 0.33 a.u. These errors are an order of magnitude smaller than the MAE (2.38 a.u.) for the $\alpha = 2/3$. The exchange functional in Eq. (1) with $\alpha = 0.7091$ is therefore better approximation than the GKS functional, at least for the atomic systems.

We now examine the performance of the HFS model for the GKS and Slater α values. The performance of the analytic HFS model in prediction of the atomization energies for the G2 set of molecules is given in Table I. The computation of atomization energies is a stringent test for computational models and has been routinely used in the appraisal of the computational models. The G2 set of molecules used in the performance analysis is the set of 54 molecules in 56 electronic states due to Pople and coworkers²⁷ and is often used for performance tests.²⁸ It is apparent from the Table I that the errors are considerably smaller for the GKS value of α than for Slater α . The atomization energies are overestimated for Slater α with a mean error of 52.4 kcal/mol while for the GKS α the molecules are by and large underbound. The minimization of the MAE leads to the α value close to 0.7. The atomization energies for the G2 set at the optimal values are also shown in Table I. Going from the GKS α to the optimal α , the MAE reduces by about 2 kcal/mol while the mean errors decreases by 6-7 kcal/mol. The reduction in the mean error mainly occurs because it changes sign for more molecules. For the GKS α , the

error is maximum (-61.49 kcal/mol) for the Si₂H₆. It is also maximal for Si₂H₆ at the optimal α . CO₂ is another molecule for which the error is comparable to this error at the optimal α .

In order to investigate the role of basis sets on the optimal α value, we optimized the α for four different basis sets. The optimal α values are 0.70650, 0.69937, 0.7032, and 0.698 for the 6311G**/RI-J, 6311G**/A2, DZVP/RI-J, and DZVP/A2, respectively. The MAE (in units of kcal/mol) at these optimal values are 13.5, 13.4, 12.8, and 12.8, respectively. All optimal values are close to 0.7 and are effectively insensitive to the orbital basis sets. A small dependence on the fitting basis set is however noticeable. The best performance is obtained for the DZVP/A2 basis set for which the MAE is 12.8 kcal/mol.

We also carried out the performance test of the model in predicting the bond distances. For this purpose we selected all (15 in total) diatomic molecules belonging to the G2 set. Our results show that the MAE in bond distances also is smaller at the optimal α value. For the 6311G**/RI-J the MAE at optimal value is 0.019 Å, 0.013 Å smaller than at the GKS α (0.032 Å). The basis set effects show that the larger 6311G**/RI-J performs better than the DZVP/A2 basis. The MAE at their optimal α values for these two bases are 0.019 and 0.048 Å, respectively. These are comparable or better than the LDA (0.024 Å) or HF (0.028 Å) errors.²⁹

In Table II we have summarized the results of present calculations. In comparison with the LDA or HF the analytic HFS model performance is significantly better. Its performance is even better than the SR-HF or the SR-Exact-Atomic models. These models are similar to the present one but make use of atom dependent α , which in case of SR-HF and SR-Exact-Atomic uses α values that give the HF atomic and the exact energies for atomic systems, respectively. The overall improvement in the performance obtained here by minimizing the MAE in atomization energies also suggest that the SR model can also be similarly improved by multidimensional minimization of MAE in the α space. There are several density functional computational schemes that use the generalized gradient approximation (GGA), the hybrid GGA or meta GGA(See for example, Ref. 19). The accuracies of these models for the G2 set range from 3-8 kcal/mol, but to date they require numerical treatment. Although its analytic implementation is computationally most efficient, the optimal values can also be used in any existing density functional code, albeit with some reduction in computational performance. It should also be borne in mind that the G2 set used in obtaining optimal α value contains small molecules consisting of atoms belonging to the first and second rows of the periodic table.

We have also examined the performance of the analytic HFS model for the extended G2 set containing 148 molecules. Reoptimizing the α in order to minimize the MAE for this larger G2 set moves optimal α significantly far in the direction of the GKS's α value. The analysis of errors for individual molecules in this dataset shows

TABLE I: The atomization energies D_0 (kcal/mol) for the 56 set of molecules for two different basis sets. The two basis sets chosen are I: 6311G**/RIJ, II: DZVP/A2. The α values are Gaspar-Kohn-Sham's alpha ($=0.66666667$), Slater's alpha ($=1.0000$), and the optimal α for which mean absolute error is minimum. The last column contains the *exact* values.

α	Basis I 0.666667	Basis I 1.00000	Basis I 0.70650	Basis II 0.666667	Basis II 1.00000	Basis II 0.69800	Exact
H ₂	81.56	91.53	82.76	84.16	94.13	84.90	103.50
LiH	33.44	48.59	34.86	30.89	41.90	31.49	56.00
BeH	46.62	79.40	50.09	25.52	46.23	27.11	46.90
CH	63.16	74.57	64.46	64.95	75.70	65.78	79.90
CH ₂ (³ B ₁)	172.67	242.62	180.69	175.69	244.94	181.41	179.60
CH ₂ (¹ A ₁)	144.13	187.45	149.03	148.50	190.34	151.92	170.60
CH ₃	269.96	359.08	280.32	274.91	362.50	282.28	289.20
CH ₄	369.54	484.63	382.87	375.72	490.08	385.38	392.50
NH	62.39	77.94	64.13	65.12	79.59	66.21	79.00
NH ₂	144.46	186.28	149.20	150.51	189.84	153.69	170.00
NH ₃	247.52	327.10	256.68	256.44	332.45	262.79	276.70
OH	91.11	116.00	94.03	94.17	116.74	96.03	101.30
H ₂ O	205.36	281.07	214.13	213.20	283.90	219.17	219.30
HF	129.94	181.58	136.01	136.08	183.42	140.19	135.20
Li ₂	6.75	7.78	6.65	5.74	9.69	5.66	24.00
LiF	127.73	200.55	135.59	118.91	192.70	124.75	137.76
C ₂ H ₂	380.64	508.89	395.62	375.39	495.61	385.98	388.90
C ₂ H ₄	514.63	688.39	534.80	519.43	688.06	534.03	531.90
C ₂ H ₆	640.65	858.65	665.79	649.78	864.88	668.10	666.30
CN	175.85	226.64	180.87	168.49	210.50	171.89	176.60
HCN	291.80	371.10	300.99	284.76	354.24	291.08	301.80
CO	262.44	327.45	269.96	251.66	307.16	257.01	256.20
HCO	279.07	370.60	289.35	274.94	359.47	282.37	270.30
H ₂ CO	357.03	476.46	370.63	356.06	469.07	365.93	357.20
CH ₃ OH	468.42	640.15	487.97	476.56	643.49	490.71	480.80
N ₂	206.16	233.59	209.47	196.84	212.00	198.89	225.10
N ₂ H ₄	371.99	512.35	387.70	386.51	519.20	397.56	405.40
NO	153.63	186.81	157.31	146.96	171.38	149.52	150.10
O ₂	144.97	191.03	149.76	141.18	183.86	145.09	118.00
H ₂ O ₂	255.11	356.29	266.06	262.57	361.22	270.64	252.30
F ₂	60.99	86.35	63.10	60.70	91.54	63.08	36.90
CO ₂	413.28	554.85	429.25	398.39	524.83	409.85	381.90
SiH ₂ (¹ A ₁)	116.69	140.69	119.57	119.85	146.07	121.96	144.40
SiH ₂ (³ B ₁)	110.16	149.90	114.64	112.65	153.60	115.87	123.40
SiH ₃	179.61	229.59	185.47	183.25	234.73	187.39	214.00
SiH ₄	260.34	326.68	268.22	264.75	333.84	270.39	302.80
PH ₂	119.12	139.95	121.62	123.02	147.19	124.89	144.70
PH ₃	191.36	229.18	195.93	197.19	240.50	200.61	227.40
H ₂ S	154.22	188.60	158.33	158.87	199.34	162.23	173.20
HCl	95.69	118.24	98.50	96.37	123.43	98.65	102.20
Na ₂	5.47	3.85	5.20	5.59	4.66	5.42	16.60
Si ₂	68.36	90.14	70.80	68.42	92.93	70.48	74.00
P ₂	91.33	101.21	92.69	91.67	103.08	92.73	116.10
S ₂	102.03	137.80	106.19	103.03	141.76	106.46	100.70
Cl ₂	57.18	92.08	60.88	58.37	95.81	61.29	57.20
NaCl	80.52	121.13	84.89	81.00	127.66	84.84	97.50
SiO	182.85	239.02	189.13	182.19	239.66	187.07	190.50
CS	165.02	202.06	169.50	163.97	202.37	167.64	169.50
SO	128.41	177.03	133.65	133.04	183.35	137.30	123.50
ClO	69.56	104.25	72.98	74.70	111.20	77.59	63.30
ClF	69.97	109.07	73.98	74.16	116.73	77.61	60.30
Si ₂ H ₆	438.03	562.19	452.72	445.26	576.48	456.04	500.10
CH ₃ Cl	361.67	484.96	375.92	366.70	492.51	377.46	371.00
H ₃ CSH	423.74	560.88	439.59	432.27	574.77	444.35	445.10
HOCl	156.11	222.91	163.21	163.22	234.11	168.94	156.30
SO ₂	250.06	356.02	261.65	254.36	360.56	263.42	254.00
mean absolute	15.9	55.2	13.5	14.5	55.3	12.8	

TABLE II: The mean absolute error (MAE) (kcal/mol) in the atomization energy of 56 molecules belonging to the G2 set is compared within different models. The numbers for the SR-HF and SR-*Exact-Atomic* are for the Slater-Roothaan model with Hartree-Fock α values and the α values that give the *exact-atomic* (See text for more details). The results of the more complex PBE GGA functional are also included for comparison.

Model	Basis	MAE
Hartree-Fock theory		78 Ref.28
LDA		36 Ref.30
PBE		8 Ref.30
SR-HF	6-311G**/RI-J	16 Ref.8
SR-HF	DZVP/A2	16 Ref.8
SR- <i>Exact-Atomic</i>	6-311G**/RI-J	19 Ref.8
SR- <i>Exact-Atomic</i>	DZVP/A2	18 Ref.8
HFS (Uniform α)	6-311G**/RI-J	14 (Present work)
HFS (Uniform α)	DZVP/A2	13 (Present work)

that this occurs due to the presence of a large percent of molecules containing fluorine in the extended G2 dataset. The errors for these molecules are lowered by decreasing the α value below 0.7. This is consistent with our earlier finding that the exact atomization of fluorine dimer is obtained for much smaller α value of 0.3.⁸ This again brings out the limitation of the uniform α HFS method and shows that the analytic SR method has a scope for improvement. It appears from the minimization of errors of the G2 and the extended G2 data sets and error analysis, as well as from the minimization of the total total

atomic energies that overall the value close to 0.7 is probably the right choice for the optimal α in the uniform α calculations.

To summarize, the performance appraisal of the analytic Hartree-Fock-Slater method is carried out for various α values using the G2 database of 56 molecules. The α value that gives the best performance is determined by minimizing the mean absolute errors in the atomization energies of the G2 set of molecules. It is shown that the analytic HFS model performs better than the LDA or HF as well as the SR method that uses atom dependent α which give the exact HF or experimental atomic energies. Further, by minimizing the MAE in the HF and the HFS total energies it is shown that the local exchange functional performs significantly better for $\alpha = 0.7091$ than the Gaspar-Kohn-Sham exchange functional. The MAE in former is an order of magnitude smaller than the MAE for the GKS exchange functional. The use of this exchange functional in more sophisticated GGAs could boost their performance considerably, and performance gain is already observed in case of Becke's exchange functional.³¹

Analytic DFT, even at this stage of development, is remarkably accurate.

The Office of Naval Research, directly and through the Naval Research Laboratory, and the Department of Defense's High Performance Computing Modernization Program, through the Common High Performance Computing Software Support Initiative Project MBD-5, supported this work.

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